

假酸浆中新的醉茄内酯类化合物*

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摘要: 从假酸浆 (*Nicandra physaloides*) 全草中分离得到 12 个化合物, 其中两个为新的醉茄内酯类化合物, 经波谱学方法将其结构鉴定为 nicandrenone methyl ether (**1**) 和 26S-nicandrenone methyl ether (**2**); 已知化合物为三个醉茄内酯, nicandrenone (**3**), Nic-7 (**4**), nicaphysalin E (**5**), 以及 pinosylvin monomethyl ether (**6**), 2S-pinocembrin (**7**), (1S, 2R)-1, 2-bis (4-hydroxy-3-methoxyphenyl)-1, 3-propanediol (**8**), vanillin (**9**), indole-3-carboxylic acid (**10**), vanillic acid (**11**) 和 drummondol (**12**)。

关键词: 假酸浆; Nicandrenone methyl ether; 26S-nicandrenone methyl ether; 醉茄内酯

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New Withanolides from *Nicandra physaloides* (Solanaceae)*YI Qian-Kun^{1,2}, LI Bo^{1**}, LIU Ji-Kai¹

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Abstract: Two new withanolides, named nicandrenone methyl ether (**1**), 26S-nicandrenone methyl ether (**2**), together with ten known compounds were isolated from the whole plants of *Nicandra physaloides* (Solanaceae). Their chemical structures were deduced on the basis of spectroscopic analysis. Ten known compounds were identified as nicandrenone (**3**), Nic-7 (**4**), nicaphysalin E (**5**), pinosylvin monomethyl ether (**6**), 2S-pinocembrin (**7**), (1S, 2R)-1, 2-bis (4-hydroxy-3-methoxyphenyl)-1, 3-propanediol (**8**), vanillin (**9**), indole-3-carboxylic acid (**10**), vanillic acid (**11**) and drummondol (**12**).

Key words: *Nicandra physaloides*; Nicandrenone methyl ether; 26S-nicandrenone methyl ether; Withanolides

Nicandra physaloides (Solanaceae) has been used as folk medicine for sedative, expectorant, fever relieving and detoxification in China (Editorial Board of National Herbal Compendium, 1975). Its seed can be utilized to extract edible pectin to make jelly. The insect antifeedant activities of its leave extract have also been reported (Ascher *et al.*, 1981, 1987). So far, more than twenty 5 α -hydroxy-6 α , 7 α -epoxy-1-oxo-2-ene type withanolides have been

obtained from the plant (Anjaneyulu *et al.*, 1997). In the course of our continuing search for bioactive natural products from Solanaceae plants, we report herein the isolation and structural elucidation of two new withanolides, nicandrenone methyl ether (**1**), 26S-nicandrenone methyl ether (**2**), together with three known withanolides, nicandrenone (**3**), Nic-7 (**4**), nicaphysalin E (**5**), and other seven known compounds, pinosylvin monomethyl ether (**6**), 2S-

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pinocembrin (**7**), (1*S*, 2*R*)-1, 2-bis (4-hydroxy-3-methoxyphenyl)-1, 3-propanediol (**8**), vanillin (**9**), indole-3-carboxylic acid (**10**), vanillic acid (**11**) and drummondol (**12**). Compounds **6**–**12** were isolated from this plant for the first time.

Results and discussion

Compound **1** was obtained as a white solid. It was assigned a molecular formula $C_{29}H_{36}O_6$ according to positive HR-ESI-MS (m/z 503.2415 $[M+Na]^+$, calc. 503.2409), and the NMR spectral analysis (Table 1). In IR spectrum, strong absorption at 1689 cm^{-1} indicated the presence of an α , β -unsaturated ketone group, which was confirmed by signals at δ_c 202.92 (C-1), 140.18 (C-2) and 128.19 (C-3) in the ^{13}C -NMR spectrum. The ^1H -NMR and ^{13}C -NMR spectra of **1** showed the presence of 29 carbons consisting of a carbonyl, four carbon-carbon double bonds, four quaternary carbons including three oxygen-bearing functional groups, seven sp^3 methines including four oxygen-bearing functional groups, four methylenes and five methyls. In ^{13}C -NMR spectra of **1**, oxygen-bearing sp^3 methines at δ_c 57.06 and 55.90 indicated the presence of 6α , 7α -epoxy moiety, oxygen-bearing quaternary carbons at δ_c 61.47 and 61.51 suggested the occurrence of 24α , 25α -epoxy moiety, oxygen-bearing sp^3 methines at δ_c 68.96 and 99.33 revealed the presence of the δ -lactol ring in the side chain. The aromatized D-ring was proved by the ^{13}C signals at δ_c 142.57, 137.15, 135.22, 128.77, 125.66, 124.08 and ^1H signals at δ_H 7.35 (*d*, 7.8), 7.06 (*d*, 7.8), 7.0 (*s*). The NMR data mentioned above suggested that it has similar structure to that of nicandrenone (Gottlieb and Kirson, 1981). The only difference between them was that the hydroxyl in nicandrenone is replaced by methoxyl (δ_c 55.70) in **1**. The HMBC spectrum of **1** showed the correlation between the signals at δ_c 99.23 (C-26) and δ_H 3.15 (OMe), and the correlation between δ_c 55.70 (OMe) and δ_H 4.55 (H-26), which confirmed the methoxyl group location at C-26 (Fig. 1). The configuration at H-22 was assigned as α -ori-

entation (0.5–4.0 Hz and 9.0–13.8 Hz for H-22 α , and 2.5–7.0 Hz and 2.0–5.0 Hz for H-22 β) for observed coupling constants of H-22 ($J=2.25$, 11.25). (Minguzzi *et al.*, 2002). In the ROESY spectrum, the cross-peak between H-26 and H-28, as well as between OMe and H-22 deduced that the methoxyl is α -orientation (Fig. 1). Thus, compound **1** was identified as nicandrenone methyl ether (Fig. 2).

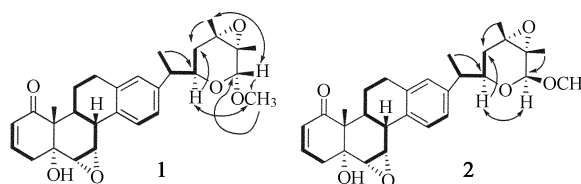


Fig. 1 Key HMBC (→), COSY (—) and ROESY (↔) correlations for compounds **1** and **2**

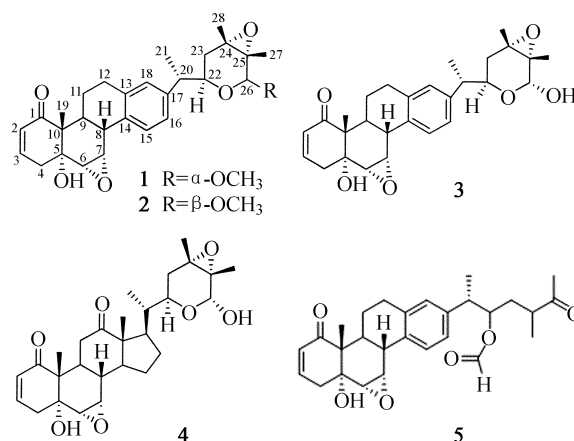


Fig. 2 Structures of compounds **1**–**5**

Compound **2** had the same molecular formula $C_{29}H_{36}O_6$ as that of compound **1**, deduced from positive HR-ESI-MS (m/z 503.2412 $[M+Na]^+$, calc. 503.2409), and the NMR spectral analysis (Table 1). ^1H - and ^{13}C -NMR spectra of **2** were very similar to those of **1**, which suggested that they have the same carbon skeleton and substituent. The configuration at C-22 was also assigned as *R* for observed coupling constants of H-22 ($J=3.20$, 11.51) (Minguzzi *et al.*, 2002). The observations of ^{13}C signal downfield shift for C-22 and C-26 (Δ 2.83, 1.72 ppm) and upfield shift for C-23 and C-27 (Δ -2.25, -3.09 ppm) suggested that methoxyl at C-26 of **2** is β -orientation. In ROESY spectrum of **2**,

the presence of correlation between H-26 (δ_{H} 4.43) and H-22 confirmed the β -orientation of methoxyl at C-26 (Fig. 1). Thus, compound **2** was identified as 26S-nicandrenone methyl ether (Fig. 2).

Compound **4** was identified as Nic-7 (nicandrenone 7) (Begley *et al.*, 1976). Its ^1H - and ^{13}C -NMR spectra data were reported for the first time. The structures of known compounds were identified by comparison of spectroscopic data with those reported in literatures.

Experimental

General experimental procedures Optical rotation was measured on a JASCO P-1020 digital polarimeter. IR spectra were obtained from Bruker Tensor 27 FT-IR spectrometer with KBr pellets. UV spectra were determined on a Shimadzu UV2401PC spectrometer. ESIMS and HRESIMS spectra were recorded on AutoSpec Premier P776 and API QSTAR Pulsar instrument. NMR spectra were recorded on Bruker AV-400 MHz, DRX-500 MHz and AVANCE III 600 MHz with TCI cryoprobe spectrometers with TMS as internal standard. Silica gel (200–300 mesh), Silica gel GF₂₅₄ (Qingdao Marine Chemical Co., Ltd), RP-18 silica gel (40–63 μm , Merck, Germany), MCI gel CHP-20P (75–150 μm , Mitsubishi Chemical Corporation, Tokyo) and Sephadex LH-20 (Pharmacia) were used for column chromatography. Fractions were monitored by TLC and spots were visualized by heating silica gel plates immersed with 10% H_2SO_4 in ethanol.

Plant material Whole plants of *N. physaloides* were collected in Kunming, Yunnan, China, in October 2009. A voucher specimen was deposited in the State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences.

Extraction and isolation Air-dried leaves of *N. physaloides* (30 kg) were extracted with methanol at 70°C for three times. The extracts were concentrated at 50–70°C to a black residue (1.8 kg) and then dissolved in H_2O , fractionated into petroleum

ether (500 g), ethyl acetate (500 g) and *n*-butanol (300 g). The ethyl acetate extract was subjected to a silica gel column using CHCl_3 : MeOH=1:0 to 2:1. Seventeen main fractions (Fr. 1-17) were obtained. By subjected to repeatedly silica gels, Sephadex LH-20, MCI and RP-18, Fr. 2 (52 g) afforded compounds **1** (30 mg), **2** (250 mg), **3** (10 g), **6** (50 mg), **7** (10 mg) and **9** (100 mg), Fr. 3 (22 g) afforded compounds **8** (13 mg), **10** (1 mg), **11** (2 mg) and **12** (2 mg), and Fr. 4 (37 g) afforded compounds **4** (40 mg) and **5** (11 mg).

Nicandrenone methyl ether (1). White crystals, $\text{C}_{29}\text{H}_{36}\text{O}_6$; Positive ESI-MS m/z : 503 $[\text{M} + \text{Na}]^+$; Positive HR-ESI-MS m/z : 503.2415 $[\text{M} + \text{Na}]^+$ (calc. 503.2409); $[\alpha]_{\text{D}}^{27.3} - 13.9$ ($c = 0.456$, CDCl_3); UV (CDCl_3) λ_{max} (log ϵ): 276 (2.82), 268 (2.88), 240 (3.33) nm; IR ν_{max} (cm^{-1}): 2924, 2853, 1689, 1632, 1457, 1394, 1379, 1104, 1054; ^1H - and ^{13}C -NMR: Table 1.

26S-nicandrenone methyl ether (2). White solid, $\text{C}_{29}\text{H}_{36}\text{O}_6$; Positive ESI-MS m/z : 503 $[\text{M} + \text{Na}]^+$; Positive HR-ESI-MS m/z : 503.2412 $[\text{M} + \text{Na}]^+$ (calc. 503.2409); $[\alpha]_{\text{D}}^{27.3} + 37.2$ ($c = 4.44$, CDCl_3); UV (CDCl_3) λ_{max} (log ϵ): 277 (2.62), 268 (2.69), 240 (3.14) nm; IR ν_{max} (cm^{-1}): 2972, 2932, 2907, 2835, 1689, 1460, 1424, 1379, 1110, 1083, 1057, 920; ^1H - and ^{13}C -NMR: Table 1.

Nicandrenone (3). Colorless crystal, $\text{C}_{28}\text{H}_{34}\text{O}_6$; Positive ESI-MS m/z : 489 $[\text{M} + \text{Na}]^+$; ^1H -NMR (CDCl_3 , 500 MHz): δ_{H} 7.31 (1H, d, $J = 8.1$ Hz, H-15), 7.01 (1H, br. d, $J = 8.1$ Hz, H-16), 6.94 (1H, s, H-18), 6.58 (1H, ddd, $J = 10.1, 5.0, 2.0$ Hz, H-3), 5.83 (1H, dd, $J = 10.1, 2.4$ Hz, H-2), 4.94 (3H, s, H-26), 3.98 (1H, br. s, H-7), 3.86 (1H, m, H-22), 3.20 (1H, d, $J = 3.9$ Hz, H-6), 3.02 (1H, d, $J = 11.6$ Hz, H-8), 2.92 (1H, m, H-12), 2.82 (1H, m, H-11), 2.79 (1H, m, H-12), 2.72 (1H, m, H-20), 2.69 (1H, m, H-4), 2.55 (1H, dd, $J = 18.9, 5.0$ Hz, H-4), 1.88 (1H, td, $J = 11.6, 3.51$ Hz, H-9), 1.81 (1H, dd, $J = 14.0, 2.2$ Hz, H-23), 1.56 (1H, m, H-23), 1.51 (1H, m, H-11), 1.33 (3H, s,

Table 1 ^1H - and ^{13}C -NMR data of **1** and **2** in CDCl_3 (δ in ppm, J in Hz)

Position	1 ^a		2 ^a	
	δ_{C}	δ_{H}	δ_{C}	δ_{H}
1	202.92 <i>s</i>		202.33 <i>s</i>	
2	128.97 <i>d</i>	5.90 (<i>d</i> , 9.9)	128.29 <i>d</i>	5.78 (<i>d</i> , 8.0)
3	140.18 <i>d</i>	6.65 (<i>dd</i> , 9.9, 4.7)	139.84 <i>d</i>	6.54 (<i>m</i>)
4	37.11 <i>t</i>	2.77 (<i>d</i> , 19.0), 2.63 (<i>dd</i> , 19.0, 4.7)	36.44 <i>t</i>	2.66 (<i>d</i> , 14.8), 2.50 (<i>dd</i> , 14.8, 4.0)
5	73.03 <i>s</i>		72.74 <i>s</i>	
6	57.06 <i>d</i>	3.26 (<i>d</i> , 3.6)	56.34 <i>d</i>	3.15 (<i>d</i> , 2.8)
7	55.90 <i>d</i>	4.06 (<i>br. s</i>)	55.76 <i>d</i>	3.94 (<i>br. s</i>)
8	38.77 <i>d</i>	3.09 (<i>d</i> , 11.0)	38.10 <i>d</i>	2.98 (<i>d</i> , 9.2)
9	32.06 <i>d</i>	1.90 (<i>td</i> , 11.0, 2.1)	31.28 <i>d</i>	1.84 (<i>m</i>)
10	51.94 <i>s</i>		51.19 <i>s</i>	
11	24.62 <i>t</i>	2.85 (<i>m</i>), 1.58 (<i>m</i>)	23.95 <i>t</i>	2.78 (<i>m</i>), 1.49 (<i>m</i>)
12	29.57 <i>t</i>	2.97 (<i>m</i>), 2.85 (<i>m</i>)	28.95 <i>t</i>	2.87 (<i>m</i>), 2.77 (<i>m</i>)
13	137.15 <i>s</i>		136.24 <i>s</i>	
14	135.22 <i>s</i>		134.75 <i>s</i>	
15	124.08 <i>d</i>	7.35 (<i>d</i> , 7.8)	123.60 <i>d</i>	7.28 (<i>d</i> , 6.4)
16	125.66 <i>d</i>	7.06 (<i>d</i> , 7.8)	124.71 <i>d</i>	6.98 (<i>d</i> , 6.4)
17	142.57 <i>s</i>		141.37 <i>s</i>	
18	128.77 <i>d</i>	7.00 (<i>s</i>)	128.10 <i>d</i>	6.91 (<i>s</i>)
19	14.31 <i>q</i>	1.26 (<i>s</i>)	13.64 <i>q</i>	1.16 (<i>s</i>)
20	43.94 <i>d</i>	2.67 (<i>m</i>)	43.50 <i>d</i>	2.69 (<i>m</i>)
21	18.40 <i>q</i>	1.23 (<i>d</i> , 8.80)	16.31 <i>q</i>	1.17 (<i>d</i> , 6.20)
22	68.96 <i>d</i>	3.93 (<i>ddd</i> , 11.25, 7.64, 2.25)	71.79 <i>d</i>	3.65 (<i>ddd</i> , 11.51, 7.01, 3.20)
23	35.52 <i>t</i>	1.97 (<i>dd</i> , 14.21, 2.25) 1.55 (<i>dd</i> , 14.21, 11.25)	33.27 <i>t</i>	1.81 (<i>m</i>) 1.72 (<i>dd</i> , 14.18, 11.51)
24	61.47 <i>s</i>		61.91 <i>s</i>	
25	61.51 <i>s</i>		60.88 <i>s</i>	
26	99.33 <i>d</i>	4.55 (<i>s</i>)	101.05 <i>d</i>	4.43 (<i>s</i>)
27	17.21 <i>q</i>	1.35 (<i>s</i>)	14.12 <i>q</i>	1.21 (<i>s</i>)
28	18.60 <i>q</i>	1.35 (<i>s</i>)	18.54 <i>q</i>	1.24 (<i>s</i>)
OCH ₃	55.70 <i>q</i>	3.15 (<i>s</i>)	55.06 <i>q</i>	3.29 (<i>s</i>)

^a At 500/125 MHz

H-27), 1.32 (3H, *s*, H-28), 1.20 (1H, *s*, H-19), 1.20 (3H, *d*, $J=7.0$ Hz, H-19); ^{13}C -NMR (CDCl_3 , 125 MHz): δ_{C} 202.66 (*s*, C-1), 128.54 (*d*, C-2), 140.02 (*d*, C-3), 36.54 (*t*, C-4), 72.55 (*s*, C-5), 56.54 (*d*, C-6), 55.28 (*d*, C-7), 38.24 (*d*, C-8), 31.38 (*d*, C-9), 51.33 (*s*, C-10), 24.06 (*t*, C-11), 29.05 (*t*, C-12), 136.61 (*s*, C-13), 134.90 (*s*, C-14), 123.78 (*d*, C-15), 125.04 (*d*, C-16), 141.15 (*s*, C-17), 128.26 (*d*, C-18), 13.79 (*q*, C-19), 42.74 (*d*, C-20), 17.03 (*q*, C-21), 67.19 (*d*, C-22), 33.43 (*t*, C-23), 64.14 (*s*, C-24), 63.16 (*s*, C-25), 91.29 (*d*, C-26), 16.30 (*q*, C-27), 18.40 (*q*, C-28). (Gottlieb and Kirson, 1981)

Nicandrenone 7 (4). White crystals, $\text{C}_{28}\text{H}_{38}\text{O}_7$; Positive ESI-MS m/z : 509 $[\text{M}+\text{Na}]^+$; ^1H -NMR (CDCl_3 , 500 MHz): δ_{H} 5.86 (1H, *d*, $J=11.5$ Hz, H-2), 6.62 (1H, *dd*, $J=11.5, 4.0$ Hz, H-3), 5.00 (1H, *s*, H-26), 3.74 (1H, *br. d*, $J=13.0$

Hz, H-22), 3.48 (1H, *dd*, $J=15.1, 4.0$ Hz, H-11), 3.40 (1H, *br. s*, H-7), 3.09 (1H, *d*, $J=4.0$ Hz, H-6), 2.70 (1H, *d*, $J=16.0$ Hz, H-4), 2.58 (1H, *dd*, $J=16.0, 4.0$ Hz, H-4), 2.52 (1H, *d*, $J=15.1$ Hz, H-11), 2.20 (1H, *br. t*, $J=13.5$ Hz, H-8), 2.03 (1H, *m*, H-17), 1.98 (1H, *m*, H-9), 1.95 (1H, *m*, H-15), 1.91 (1H, *m*, H-23), 1.81 (1H, *m*, H-16), 1.77 (1H, *m*, H-23), 1.63 (1H, *m*, H-14), 1.60 (1H, *m*, H-15), 1.60 (1H, *m*, H-20), 1.47 (1H, *m*, H-16), 1.43 (3H, *s*, H-27), 1.43 (3H, *s*, H-28), 1.24 (3H, *s*, H-18), 1.08 (3H, *s*, H-19), 0.87 (3H, *d*, $J=8.0$ Hz, H-21); ^{13}C -NMR (CDCl_3 , 125 MHz): δ_{C} 201.42 (*s*, C-1), 128.76 (*d*, C-2), 139.87 (*d*, C-3), 36.54 (*t*, C-4), 73.15 (*s*, C-5), 56.09 (*d*, C-6), 56.93 (*d*, C-7), 35.48 (*d*, C-8), 37.47 (*d*, C-9), 51.39 (*s*, C-10), 38.26 (*t*, C-11), 212.48 (*s*, C-12), 57.62 (*s*, C-13), 52.70 (*d*, C-14), 23.58 (*t*,

C-15), 26.83 (t, C-16), 42.96 (d, C-17), 14.69 (q, C-18), 11.43 (q, C-19), 39.66 (d, C-20), 12.85 (q, C-21), 65.05 (d, C-22), 29.48 (t, C-23), 65.44 (s, C-24), 63.90 (s, C-25), 91.72 (d, C-26), 16.54 (q, C-27), 18.97 (q, C-28). (Gottlieb and Kirson, 1981)

Nicaphysalin E (5). White crystals, $C_{28}H_{34}O_6$; Positive ESI-MS m/z : 489 $[M+Na]^+$; 1H -NMR ($CDCl_3$, 500 MHz): δ_H 5.82 (1H, d, $J=10.0$ Hz, H-2), 7.93 (1H, s, H-CHO), 7.29 (1H, d, $J=7.30$ Hz, H-15), 7.00 (1H, d, $J=7.30$ Hz, H-16), 6.92 (3H, s, H-18), 6.75 (1H, dd, $J=10.0, 5.0$ Hz, H-3), 5.07 (1H, m, H-22), 3.98 (1H, br. s, H-7), 3.19 (1H, d, $J=3.0$ Hz, H-6), 3.06 (1H, d, $J=11.0$ Hz, H-8), 2.90 (1H, m, H-12), 2.85 (1H, m, H-20), 2.80 (1H, m, H-11), 2.80 (1H, m, H-12), 2.70 (1H, d, $J=19.0$ Hz, H-4), 2.55 (1H, dd, $J=19.0, 5.0$ Hz, H-4), 2.05 (3H, s, H-26), 1.99 (1H, m, H-23), 1.85 (1H, br. t, $J=11.0$ Hz, H-9), 1.52 (1H, m, H-11), 1.31 (1H, m, H-23), 1.20 (3H, d, $J=6.5$ Hz, H-21), 1.19 (3H, s, H-19), 1.00 (3H, d, $J=6.0$ Hz, H-28); ^{13}C -NMR ($CDCl_3$, 125 MHz): δ_C 202.66 (s, C-1), 128.57 (d, C-2), 140.10 (d, C-3), 36.82 (t, C-4), 72.75 (s, C-5), 56.78 (d, C-6), 55.48 (d, C-7), 38.50 (d, C-8), 31.64 (d, C-9), 51.60 (s, C-10), 24.26 (t, C-11), 29.26 (t, C-12), 137.08 (s, C-13), 135.61 (s, C-14), 124.14 (d, C-15), 125.17 (d, C-16), 140.24 (s, C-17), 128.70 (d, C-18), 13.99 (q, C-19), 43.35 (d, C-20), 17.59 (q, C-21), 75.69 (d, C-22), 34.84 (t, C-23), 42.97 (d, C-24), 211.52 (s, C-25), 28.56 (q, C-26), 17.70 (q, C-28), 160.84 (d, CHO). (Shingu *et al.*, 1994)

Pinosylvin monomethyl ether (6). White powder, $C_{15}H_{14}O_2$; 1H -NMR ($CDCl_3$, 500 MHz): δ_H 7.48 (2H, d, $J=7.41$ Hz, H-2', 6'), 7.35 (2H, t, $J=7.41$ Hz, H-3', 5'), 7.27 (1H, t, $J=7.41$ Hz, H-4'), 7.04 (1H, d, $J=16.23$ Hz, H-8), 6.98 (1H, d, $J=16.23$ Hz, H-7), 6.68 (1H, s, H-6), 6.64 (1H, s, H-2), 6.40 (1H, s, H-4), 3.79 (3H, s, OMe); ^{13}C -NMR ($CDCl_3$, 125

MHz): δ_C 160.99 (s, C-3), 156.87 (s, C-5), 139.83 (s, C-1), 137.06 (s, C-1'), 129.49 (d, C-8), 128.77 (d, C-3', 5'), 128.30 (d, C-7), 127.88 (d, C-4'), 126.71 (d, C-2', 6'), 106.26 (d, C-2), 105.10 (d, C-6), 101.17 (d, C-4), 55.49 (d, OMe). (Luk *et al.*, 1983).

2S-pincembrin (7). White powder, $C_{15}H_{14}O_4$; $[\alpha]_D^{18.2} -16.2$ ($c=0.11$, MeOH); 1H -NMR ($CDCl_3$, 500 MHz): δ_H 7.44 (2H, m, H-2', 6'), 7.41 (2H, m, H-3', 5'), 7.37 (1H, m, H-4'), 5.97 (2H, d, $J=0.86$ Hz, H-7, 9), 5.38 (1H, dd, $J=3.05, 13.05$ Hz, H-3), 3.06 (1H, dd, $J=13.05, 17.16$ Hz, H-4), 2.77 (1H, dd, $J=3.05, 17.16$ Hz, H-4); ^{13}C -NMR ($CDCl_3$, 125 MHz): δ_C 195.63 (s, C-4), 166.70 (s, C-8), 163.83 (s, C-6), 163.09 (s, C-10), 138.42 (s, C-1'), 128.84 (d, C-3', 4', 5'), 126.16 (d, C-2', 6'), 102.46 (s, C-5), 96.55 (d, C-7), 95.67 (d, C-9), 79.11 (d, C-2), 43.27 (d, C-3). (Yuan *et al.*, 2008)

(1S,2R)-1,2-bis(4-hydroxy-3-methoxyphenyl)-1,3-propanediol (8). White powder, $C_{17}H_{20}O_6$; $[\alpha]_D^{12.3} +0.27$ ($c=1.95$, MeOH); 1H -NMR (CD_3OD , 500 MHz): δ_H 6.71 (1H, d, $J=3.22$ Hz, H-2'), 6.69 (1H, d, $J=3.28$ Hz, H-2''), 6.64 (4H, m, H-5', 5'', 6', 6''), 4.92 (1H, d, $J=6.54$ Hz, H-1), 3.83 (1H, dd, $J=6.54, 10.70$ Hz, H-3), 3.76 (3H, s, H-OMe(3'')), 3.69 (3H, s, H-OMe(3')), 3.68 (1H, m, H-3), 2.91 (1H, q, $J=6.54$ Hz, H-2); ^{13}C -NMR (CD_3OD , 125 MHz): δ_C 75.62 (d, C-1), 56.90 (d, C-2), 64.57 (t, C-3), 136.59 (s, C-1'), 111.60 (d, C-2'), 148.59 (s, C-3'), 146.69 (s, C-4'), 115.76 (d, C-5'), 120.43 (d, C-6'), 132.39 (s, C-1''), 114.57 (d, C-2''), 148.49 (s, C-3''), 146.27 (s, C-4''), 115.55 (d, C-5''), 123.24 (d, C-6''), 56.26 (q, C-3'), 56.38 (q, C-3''). (Kazuko *et al.*, 1998)

Vanillin (9). White powder, $C_8H_8O_3$; 1H -NMR ($CDCl_3$, 500 MHz): δ_H 9.82 (1H, s, H-7), 7.45 (2H, m, H-2, 6), 7.06 (1H, d, $J=8.41$ Hz, H-5), 3.93 (3H, s, H-OMe(3)); ^{13}C -NMR ($CDCl_3$, 125 MHz): δ_C 129.58 (s, C-1), 109.06 (d, C-2), 147.39 (s, C-3), 152.09 (s, C-4), 114.65 (d, C-

5), 127.62 (d, C-6), 191.34 (d, C-7), 56.03 (d, C-OMe(3)). (Hu and Zheng, 2005)

Indole-3-carboxylic acid (10). White powder, $C_9H_7NO_2$; Positive ESI-MS m/z : 184 $[M + Na]^+$; 1H -NMR ($CDCl_3$ (CD_3OD added), 500 MHz): δ_H 8.16 (1H, dd, $J=3.05, 5.87$ Hz, H-5), 7.95 (1H, s, H-2), 7.45 (1H, dd, $J=3.11, 5.92$ Hz, H-8), 7.25 (2H, m, H-6, 7); ^{13}C -NMR ($CDCl_3$ (CD_3OD added), 125 MHz): δ_C 132.41 (d, C-2), 107.74 (s, C-3), 136.58 (s, C-4), 121.20 (d, C-5), 122.68 (d, C-6), 121.62 (d, C-7), 111.88 (d, C-8), 126.18 (s, C-9), 168.27 (s, C-10). (Shaheen *et al.*, 1987)

Vanillic acid (11). White powder, $C_8H_8O_4$; Positive ESI-MS m/z : 191 $[M + Na]^+$; 1H -NMR (CD_3OD , 500 MHz): δ_H 7.57 (1H, d, $J=8.64$ Hz, H-6), 7.56 (1H, s, H-2), 6.84 (1H, d, $J=8.64$ Hz, H-5), 3.89 (3H, s, H-8); ^{13}C -NMR (CD_3OD , 125 MHz): δ_C 123.12 (s, C-1), 115.77 (d, C-2), 148.57 (s, C-3), 152.55 (s, C-4), 113.74 (d, C-5), 125.22 (d, C-6), 170.14 (s, C-7), 56.33 (s, C-8). (Zou and Yang, 2005)

Drummondol (12). White powder, $C_{13}H_{20}O_4$; 1H -NMR ($CDCl_3$, 500 MHz): δ_H 6.16 (1H, dd, $J=6.37, 15.25$ Hz, H-2'), 5.85 (1H, dd, $J=1.16, 15.25$ Hz, H-1'), 4.39 (1H, p, $J=6.37$ Hz, H-3'), 3.84 (1H, dd, $J=2.93, 8.22$ Hz, H-7), 3.70 (1H, d, $J=8.22$ Hz, H-7), 2.55 (2H, br. s, H-4), 2.51 (1H, dd, $J=2.84, 18.41$ Hz, H-2), 2.37 (1H, d, $J=18.41$ Hz, H-2), 1.27 (3H, d, $J=6.37$ Hz, H-Me(3')), 1.13 (3H, s, H-Me(5)), 0.94 (3H, s, H-Me(1)); ^{13}C -NMR ($CDCl_3$, 125 MHz): δ_C 47.84 (s, C-1), 52.61 (t, C-2), 208.68 (s, C-3), 52.77 (t, C-4), 81.86 (s, C-5), 77.23 (t, C-7), 85.68 (s, C-8), 123.77 (d, C-1'), 139.98 (d, C-2'), 68.34 (d, C-3'), 15.80 (q, C-Me(1)), 24.23 (q, C-Me(3')), 18.87 (q, C-Me(5)). (Powell and Smith, 1981)

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